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Thermal stability of electron traps in GaN grown by metalorganic chemical vapor deposition

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Deep level transient spectroscopy was used to investigate the thermal stability of electron traps in *n*-type GaN grown by metalorganic chemical vapor deposition. The concentration of traps at 160 and at 500 K increased more than fivefold over the course of several 700 K anneal cycles, while a peak at 320 K increased by a factor of only 1.19. The increase in the trap concentration with repeated annealing might be due to a mobile trap or loss of passivant. Hydrogen is very likely present in high concentration in the epilayer, and its passivating effects may be lost with annealing. © 2004 American Institute of Physics. [DOI: 10.1063/1.1814801]

The thermal stability of defects in GaN is a topic of concern in the reliability of many types of devices including high power and high temperature transistors, ultraviolet sensing, and ultraviolet and visible emitters. The lack of native substrate makes the fabrication of efficient and reliable devices particularly difficult, where growth on sapphire typically results in a dislocation density of $10^{10}/\text{cm}^2$ unless special precautions are taken.¹ Propagation of threading dislocations through active layers of electronic devices has been reported to limit two-dimensional electron gas mobility by providing charged scattering centers and boundary scattering.² Moreover, the dislocations provide parasitic current paths,^{3–5} decreasing the gain and increasing the noise in electronic devices, increasing the threshold current and decreasing the slope efficiency of lasers, and reducing the responsivity of detectors, as well as introducing instabilities particularly in devices relying on charge control and high electric fields, such as field effect transistors. If the defects that act as traps, recombination or generation centers, and scattering centers change in character under device operating conditions, they could have a detrimental impact on the reliability of the device. The thermal stability depends on the formation energy and diffusion energy.

The energy of formation of native defects and their diffusion energies have been calculated, and depend on the type and density of carriers at the growth temperature.⁶ Gallium vacancies are favored for *n*-type GaN, and nitrogen vacancies are strongly favored in *p*-type GaN. The V_{Ga} is expected to be most stable in its 3^- charge state, and acts as a triple acceptor. Other native defects are unlikely due to much higher formation energies under equilibrium conditions, which may or may not be achieved. The diffusion energy of the V_{Ga} is 1.9 eV, and 2.6 eV for a V_{N} , but only 1.2 eV for a Ga_i . Also, according to Ref. 6 there is a metastable position for the Ga_i with a barrier of only 0.9 eV. As another example, beryllium diffuses in the *c*-plane with diffusion energy of 1.2 eV, compared to diffusion energy of 2.9 eV along the *c* axis.⁷ Another consideration is that dislocations may act as sources for native defects, e.g., growth of *n*-type

GaN under gallium rich conditions may encourage formation of either type of vacancy at dislocations,⁸ which can then disperse within the crystal if the diffusion energy is low enough. With potentially low and anisotropic diffusion energies, we may expect that some of the defects in GaN are mobile at moderately high temperatures, within device operational range. Electron traps that have been characterized by deep level transient spectroscopy are 0.14,^{9,10} 0.18–0.30,^{9–20} 0.49–0.61,^{9–12,15,16,18–21} 0.65–0.67,^{9,12,16,18,20} 0.72–0.78,^{10,13,15,18} 0.89–0.96,^{10,13,15,18,20} and 1.63 eV,⁹ some of which have been attributed to specific defects. In this letter we characterize and discuss the thermal stability of electron traps in *n*-GaN grown by metalorganic chemical vapor deposition (MOCVD).

The GaN epilayers that were investigated were grown in a MOCVD system at a pressure of 200 Torr, on *c*-plane sapphire ($\alpha\text{-Al}_2\text{O}_3$). Trimethylgallium (TMG) and ammonia (NH_3) were used as sources of Ga and N, respectively. The substrate was preheated in a stream of H_2 at 1030 °C for 3 min, on which a 30-nm-thick GaN buffer layer was grown at 550 °C. This was followed by the growth of a 2.4- μm -thick GaN epilayer at 1010 °C. The layers were doped with Si to $1.5 \times 10^{17}/\text{cm}^3$. The flow rates of the TMG, NH_3 , and H_2 used in the growth of GaN were 78.58, 316, and 286 mmol/min, respectively. The resulting GaN films are Ga polar.

The samples were cleaned in acetone, methanol, and de-ionized water. HCl was used to remove the oxide layer. Ohmic contacts were formed by depositing Ti/Al/Ti/Au(300 Å/300 Å/150 Å) in a vacuum of better than 4×10^{-7} Torr and annealed at 900 °C for 1 min by rapid thermal annealing in nitrogen ambient. Schottky contacts were from Ni/Au(300 Å/750 Å), 250 μm in diameter. The diodes had series resistances in the range of 20–40 Ω .

The deep level transient spectroscopy (DLTS) system is based on a SULA capacitance meter, with the transients digitized for subsequent processing to generate the spectra, and fitting for emission rate and amplitude. The signal to noise ratio is significantly improved by averaging several thousand transients at each temperature step. The temperature is incremented by 3 K from 80 up to 700 K. Compared to typical DLTS systems that use ratewindow analysis, at temperatures

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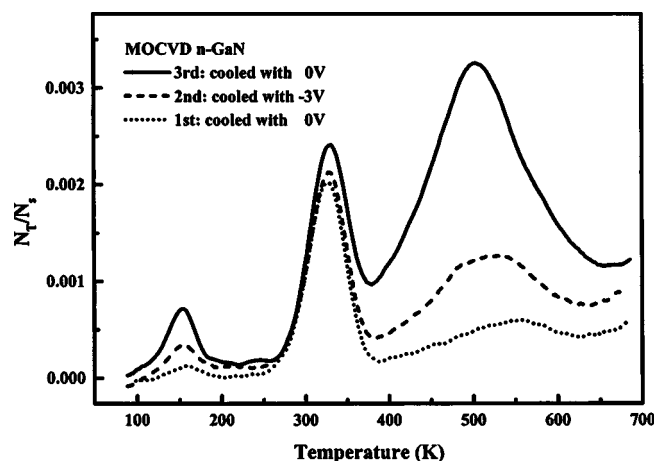


FIG. 1. Deep level spectra for MOCVD GaN showing an increase in trap concentrations with repeated cycling to 700 K. The effects of bias during cooling from 700 K were secondary to the effects of heating.

up to only 425 K, this system has better sensitivity to overlapping trap signals, and deeper traps.

The DLTS spectra taken under various bias conditions during cooling from 700 K are shown in Fig. 1. Standard ratewindow analysis for the peak at 150 K gave a trap signature of 0.25 eV activation energy and, $5.5 \times 10^{-16} \text{ cm}^2$ capture cross section. However, spectra simulated from the trap signature obtained from the ratewindow analysis did not compare well to the experimental data, being at the correct temperature but too narrow. From a fit of the transients, which was best for two components, the peak at 150 K consists of traps at 0.10 and 0.14 eV, with capture cross sections of 7×10^{-21} and $4.5 \times 10^{-19} \text{ cm}^2$, respectively. The peak at 320 K, in the spectrum measured at -1 V, had an energy of 0.55 eV and capture cross section of $6 \times 10^{-16} \text{ cm}^2$ using either method. At -3 V measurement bias, the ratewindow analysis gave an energy of 0.48 eV, and exponential fitting gave a slightly better fit for two traps at 0.43 eV, $2 \times 10^{-17} \text{ cm}^2$, and 0.34 eV, $3 \times 10^{-19} \text{ cm}^2$. The second trap may have been more easily detected at the higher measurement bias due to the larger volume scanned. The reduction in energy, from 0.55 down to 0.48, or 0.43 eV, at larger reverse bias indicates a Poole-Frenkel barrier lowering which is characteristic of a donor trap potential profile, subject to further detailed measurements given later. A ratewindow analysis of the broad peak at 500 K gave an energy of 0.87 eV, $4 \times 10^{-16} \text{ cm}^2$ at high emission rates (higher temperatures). Two peaks were distinguishable at smaller emission rates ($<200/\text{s}$), resulting in a measured trap energy of 0.62 eV, and capture cross section of $2 \times 10^{-18} \text{ cm}^2$, and a trap at around 1.2 eV, $3 \times 10^{-14} \text{ cm}^2$. However, fitting of the transients for two components did not result in linear Arrhenius plots, indicating that there may be more than two components, or an emission mechanism other than thermionic.

Measurements were also made to determine if the traps showed a metastable behavior similar to the results of Aurret *et al.* (Ref. 17) in hydride vapor phase epitaxy (HVPE) GaN. However, as the measurements were repeated on the same diode, all of the traps appeared to increase in concentration, especially the peaks centered at 150 and 500 K. The ratio of the final to initial peak height is 5.65 for the peak at 150 K, 1.19 for the peak at 320 K, and 5.43 for the peak at 500 K.

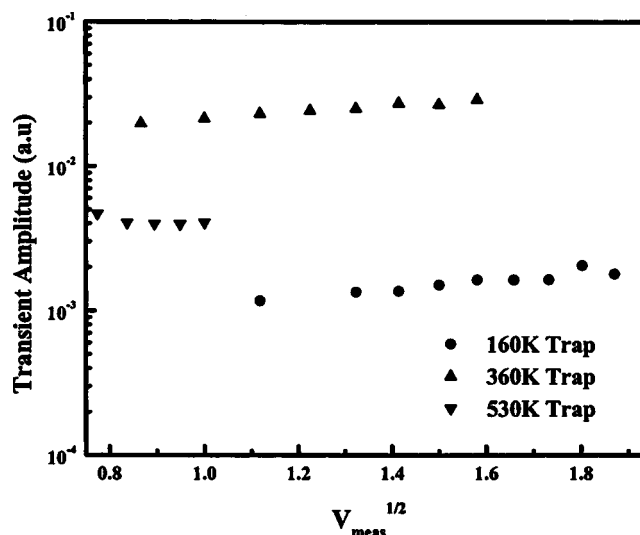


FIG. 2. Deep level profiles for each of the peaks shown in Fig. 1. Uniform depth profile for each trap indicates that they do not result from diffusion from either the contact surface or the substrate side of the epilayer during annealing.

One possibility for this behavior is a change in the contact or epilayer resistivity that would simply change the sensitivity of measurements. The I - V relationship was measured prior to each DLTS scan to obtain the series resistance. The series resistance did not change appreciably, varying from 35, 27, and 31 Ω , respectively.

Further DLTS investigations characterized the defect spatial and potential profiles, and the capture kinetics. Pairs of filling and measurement biases were used to characterize the change in trap concentration with depletion width for the three peaks. Figure 2 is a plot of the transient amplitudes normalized to the scanned volume versus square root of applied bias, which is proportional to the depletion width. The defects all showed uniform concentration, within the confidence of the capacitance-voltage profiles that were used to normalize the capacitance transient amplitudes.

The emission rate was also measured as a function of measurement bias to indicate the charge state after emission. There was an increase in emission rate with increasing reverse bias indicating a donor trap nature for the traps at 320 K, but not for the peaks at 150 or 500 K. The increase in emission rate with electric field was less than expected for a trap with a 1+ charge after emission, but the electric field was averaged over a wide range in the depletion region.

To determine if there is a capture barrier, the filling pulse was increased from 1 to 100 ms at temperatures of 140, 330 and 500 K. The temperatures were chosen to obtain low emission rates in order to increase the likelihood of seeing a change in concentration of filled traps within the range of filling pulse durations used. However, the transient amplitudes did not change, indicating there are no significant capture barriers related to lattice relaxation or line defects. Several of the native defects are predicted to have a significant lattice relaxation as a result of a change of charge state.⁶

The increase in the trap concentration with repeated annealing at 700 K might be due to a mobile species present either as a trap or as a passivant. Mobile defects could be diffusing from the substrate-epilayer interface, from the contact metalization, or from defect clusters or dislocations. The n -type GaN was grown under gallium rich conditions, which

could encourage formation of either gallium or nitrogen vacancies at dislocations, although the formation energy is high enough that the concentration should be negligible unless growth conditions are far from equilibrium.⁸ Of the two, only the nitrogen vacancy would behave as an electron trap. However, the diffusion energy of the nitrogen vacancy is too high to have an appreciable effect at 700 K. Hydrogen is known to have a high concentration in molecular beam epitaxy (MBE) and MOCVD GaN, and to passivate defects.^{22,23} H⁺ implanted into GaN creates infrared absorption bands, all of which anneal out by 650 °C, although the frequencies observed were attributed to V_{Ga}-H complexes.²⁴ Ammonia that is not fully dissociated can be a source of hydrogen, with a concentration in the range of $9 \times 10^{20}/\text{cm}^3$ as measured by nuclear reaction analysis in MBE GaN.²³ GaN exposed to hydrogen plasma showed deep level concentrations reduced by a factor of 4.7, measured by thermally stimulated current at temperatures below 350 K.²² The passivation of deep levels by hydrogen remained until an anneal temperature of 900 °C was reached. In other work, the concentration of one of three traps found in HVPE GaN, corresponding to the trap at 320 K in Fig. 1, was found to increase when annealed from 370 K under reverse bias, and decrease when annealed from 370 K, under zero bias.¹⁶ The bias annealing effect was attributed to hydrogen dissociation and reversible motion of hydrogen into and out of the bulk, controlled by the electric field. For the MOCVD sample characterized in the present study, the change was of the same size as in Ref. 16 for the trap at 320 K but the effect is not reversible in our case. Furthermore, the increase in concentration of the other two peaks with annealing at 700 K is a much larger effect, over 500%, compared to 20% for the trap at 320 K. The differences in annealing behavior may be due to the differences in growth method and growth temperature, where HVPE was used in Ref. 16.

From the DLTS measurements presented here, trap passivation is lost at a temperature below 425 °C. This work further investigates previous bias annealing measurements to higher temperatures for deeper traps.¹⁶ Also, annealing at higher temperatures than previously used, identified a more significant effect on trap concentration than bias annealing. The concentration of traps at 150 and 500 K increased by a factor greater than 5 over the course of several 700 K anneals. The deep level profiles showed a uniform concentration of each of the deep levels, indicating that the source is not an impurity diffusing either from the substrate or from the contact surface. None of the traps showed capture behavior related to threading dislocations of lattice relaxation. Only the trap at 300 K exhibited an increase in emission rate at higher electric fields, indicating a donor nature. Hydrogen

is very likely present in high concentration in the epilayer, and may be responsible for the change in defect concentration with annealing. Previous works have shown various hydrogen effects at various threshold temperatures, suggesting several mechanisms such as loss from the surface region, or dissociation of hydrogen from complexes with a variety of species.

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